

## SYNTHESIS AND CHARACTERIZATION OF BRIDGED PHTHALOCYANINE & TETRAPYRAZINO PORPHYRAZINE COMPLEXES OF ALUMINUM AND THEIR COPOLYMER

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### ABSTRACT

A two types of bridged complexes of Aluminum with two types of ligands phthalocynine and tetrapyrazino Porphrazine were prepared according to an adjusted procedure as in the literatures <sup>(1,2)</sup> to forms a two complexes Phthalocyanine to separately Aluminum chloride[I] and tetrapyrazino Porphrazine Aluminum chloride[II] then converted separately to phthalocyanato Aluminum hydroxide [III] and tetrapyrazino Porphrazine Aluminum hydroxide[IV]. The hydroxide complexes then converted to the bridged polymeric fluoride complexes [V] and [VI]. Their copolymer [VII] were prepared from the mixture of hydroxide complexes [III] and [IV] of(1:1) ratio to the polymeric fluoride of two ligands. The compounds then characterized by elemental analysis and spectroscopic methods.

#### ملخص البحث:

يتضمن البحث تحضير نوعين من المعقدات البوليمرية الجسرية للألومنيوم مع مجموعتين من الفثالوسيانين ورباعي الباييرازين البورافرازين ، كما حضر البوليمر المشترك لهذه المعقدات. وشخصت هذه البوليمرات المعقدة بالتحليل العنصري الدقيق والطرق الطيفية المختلفة ، تحت الحرارة ، المرئية وفوق البنفسجية ، والرنين النووي المغناطيسي.

**KEYWORDS:** Bridged Aluminum Phthalocynine and Tetrapyrazino Porphrazine Complexes Abridged Copolymer

### INTRODUCTION

Tetrapyrrole macro cycles such as phthalocyanine, porphyrines and porphyrazines, posses a conjugated of 18  $\pi$  - electrons . The presence of a  $\pi$ -electron system is essential for charge-carrier transport, so they exhibit a number of unique properties which bring a great interest in several scientific and technological areas ranging from nanotechnology to medicine<sup>[1]</sup>.

There has been growing interest in the use of tetrapyrrole macro cycles in variety of new high technology fields including energy conversion electrophotography, gas sensors, liquid crystals, infrared dyes for laser technology optical data storage, Semiconductor devises. Langmuir – Brosgett films, electro chromic display devises. Non-linear optics, organic light emitting diodes( OLED). Photodynamic cancer therapy(PDT) and various catalytic processes.<sup>[2]</sup>

Phthalocyanine and tetrapyrazinoporphrazin rings may either be separate units such as metal free, metallic phthalocyanine or linked with other phthalocyanine rings in the form of dimmer, oligomers or polymers. There are three known types of linkages in phthalocyanine. <sup>[3]</sup>

- Dimeric forms have the metal sandwiched between the two phthalocyanine rings .this kind of linkage is found in the phthalocyanine complex of lanthanides and actinides.<sup>[4]</sup>

- A two dimension eka-linked phthalocyanine polymer, these materials are usually prepared from tetracyano benzene where the macro cycles are linked via the peripheral conjugated systems to give a layer type structure. <sup>[5]</sup>.
- $\mu$  – Bridged phthalocyanine polymers, where a ligand is used which can act a bridge between two macro cycles via the central metal atoms. <sup>[6]</sup>. This will give cofacially stacked face to face phthalocyanine units with a rigid structure. Several different types of ligands are used to act as bridging units, such as F( $\mu$  - fluoro), O( $\mu$  -oxo), CN ( $\mu$  -cyano), pyrazine (pyz) and others. <sup>[7]</sup>.

Our work is including the third type of linkage as polymer and copolymer.

## EXPERIMENTAL

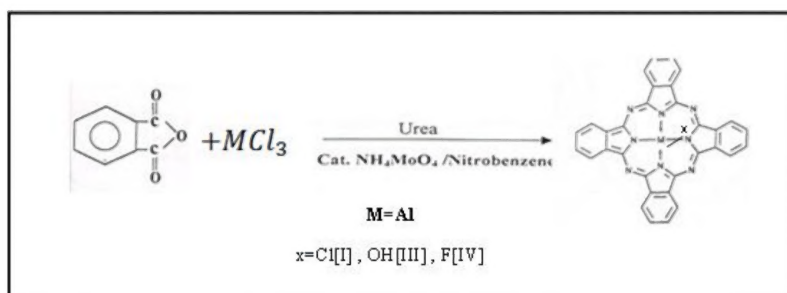
### • Chemical Materials

The chemicals were used as it was supplied except pyridine and Quinonline which were distilled twice for each

### • Synthesis of Phthalocynine Compounds

#### • Phthalocyninato Aluminum Chloride AlPcCl [I] <sup>[8,9]</sup>

A mixture phthalic anhydride(4.50g, 0.04mol), Aluminum chloride( 1.33g,0.01mol), urea( 8g), ammonium molybdate( 0.01g) and nitro benzene(50ml) was refluxed for 5 hours the reaction mixture was then cooled and filtered and washed with Ethanol, acetone,  $\text{CCl}_4$ . The crude reaction products were purified by reflux with ( 100ml) of 1N of each HCl, NaOH sequences and the washed with hot water and dried at  $110^\circ\text{C}$ . The yield is dark blue powder ( 3g, 68%) of AlPcCl.



**Figure 1: Synthesis of AlPcCl**

#### • Phthalocyninato Aluminum Fluoride (Al Pc F)<sub>N</sub>[V]:

A mixture AlPcCl(1.5g), ammonium hydroxide 25ml (25%) and pyridine (50ml) was refluxed for 7 hours. The resulting solid was filtered, washed with conc ammonium hydroxide and water dried at  $110^\circ\text{C}$  assumed to be AlPc.OH.[III] . A portion of this product (1g) was evaporated to dryness on a steam bath (using plastic dish) with three separate portions of (40%) hydrofluoric acid (4 ml each tim). The resulting solid was washed with water, acetone, and dried at  $110^\circ\text{C}$ . The yield (0.9g, 62%) of (AlPcF)<sub>n</sub> [V] as dark blue powder.

CHN: calculated ( $\text{C}_{32}\text{H}_{16}\text{N}_8 \text{AlF}$ )<sub>n</sub> C:68.81, H: 2.86, N: 20.07; Found C:68.10, H: 3.00, N: 20.59.

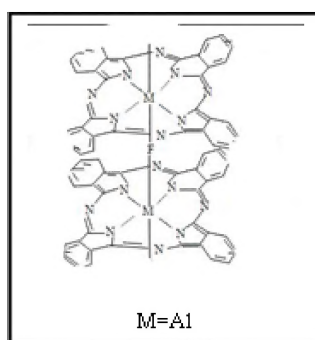


Figure 2: Synthesis of (PcAlF)

- **Synthesis of Porphyrizine Compounds**

- **Synthesis of 2,3-Dicyano Pyrazine<sup>[1,9]</sup> (PN)**

A (1ml) of glyoxal was dissolved in 25 ml ethanol and 25 ml dropwise is of acetic acid and then added into conical flask filtered with condenser containing (2.36g, 0.0218mol) diamino malonetrile ( DAMN) dissolved in 25 ml ethanol. The mixture was then refluxed for 4 hours and left for two day to settle down. The precipitate then filtered and recrystallized from mixture of hexane and acetone (1:1) ratio. The yield (0.73, 35%) of 2,3-dicyano pyrazine as dark brown powder.

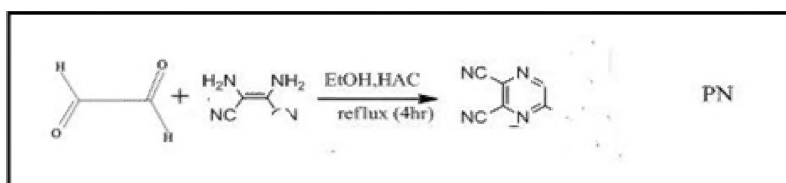


Figure 3: Synthesis of PN

- **Synthesis of Tetra Pyrazino Porphyrizine Aluminum Chloride (Alpzcl)[II]**

A mixture of Aluminum chloride anhydrous ( $0.133\text{g}$ ,  $8 \times 10^{-4}$  Mol), 2,3- dicyano- pyrazine (  $1.12\text{g}$ ,  $4 \times 10^{-3}$ mol), Urea ( $1.5\text{g}$ ,  $4.5 \times 10^{-4}$ mol), 8 ml quinoline was refluxed for 4 hours, The reaction mixture was left till evaporation of the whole solvent, The crude reaction product was purified by dissolving it in chloroform, then adding the solution dropwise with stirring to a beaker continuing ethanol. The precipitated was then filtered of and dried at  $110^\circ\text{C}$ . The yield is ( $0.26\text{g}$ , 63%) of (AlPz Cl) as a dark brown powder.

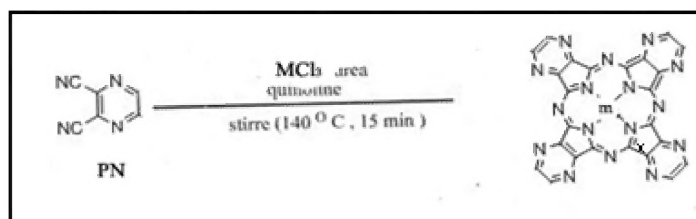


Figure 4: Synthesis of AlPzCl

- **Synthesis of tetra pyrazino porphyrizine Aluminum Fluoride (Al Pz F)<sub>n</sub>[VI]**

A mixture of (AlPz Cl) ( $1.5\text{g}$ ,  $2.5 \times 10^{-3}$ mol), ammonium hydroxide 25 ml (25%) and pyridine 50 ml were refluxed for 7 hours. The resulting solid was filtered, washed with conc. ammonium hydroxide hot water and dried at  $110^\circ\text{C}$

assumed to be  $\text{AlPzOH[IV]}$ . A portion of this product (1g) was placed on a plastic dish and evaporated to dryness on a steam bath with three separate portions of 40% hydrofluoric acid (20ml each time). The resulting solid was dried at  $110^\circ\text{C}$ . The product was a dark brown powder. The yield is (0.85g, 60%) as  $(\text{Al Pz F})_n\text{[VI]}$ .

CHN: Calculated  $(\text{C}_{24}\text{H}_8\text{N}_{16}\text{FeF})_n$  C: 50.88, H: 1.41, N: 39.57; Found : C: 50.38, H : 1.07, N: 39.06.

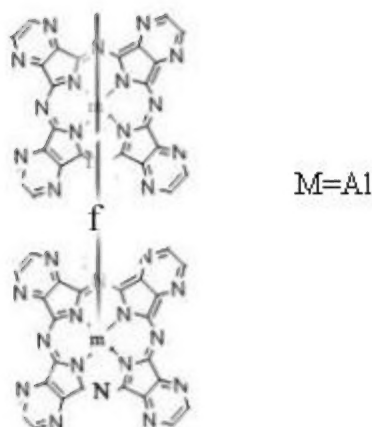


Figure 5: Synthesis of  $(\text{Al Pz F})_n$

- **Synthesis of A Copolymer of  $(\text{Al PcF- Al PzF})_n\text{[VII]}$**

A mixture of  $\text{AlPcOH}$ . (0.5g, 0.001mol)<sup>[9]</sup> and  $\text{AlPz OH}$ . ( 0.5g, 0.001mol) was refluxed with Ethanol for 15min to ensure better mixing then evaporated to dryness on a steam bath(using a plastic dish) with hydrofluoric acid for three times (2 ml each time). The resulting solid was washed with acetone, water and dried at  $110^\circ\text{C}$ . The yield is 0.45g of  $(\text{Al pcF- Alpz F})_n$  as a dark blue powder. CHN: Calculated  $(\text{PcAlF-AlPzF})_n$  C: 59.78, H: 2.13, N: 29.89; found: C: 59.12,H:1.80 N:29.47

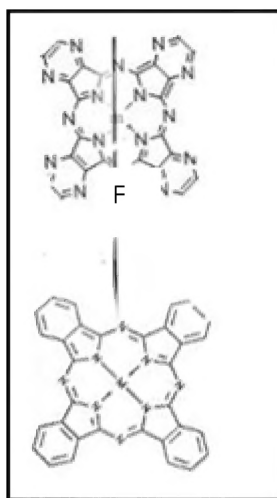


Figure 6: Synthesis of  $(\text{Al PcF-AlPz F})_n$

## RESULTS AND DISCUSSIONS

- **Infra-Red Spectra( I. R)**

The IR data of these complexes display characteristic bands for the main functional groups at certain frequencies.

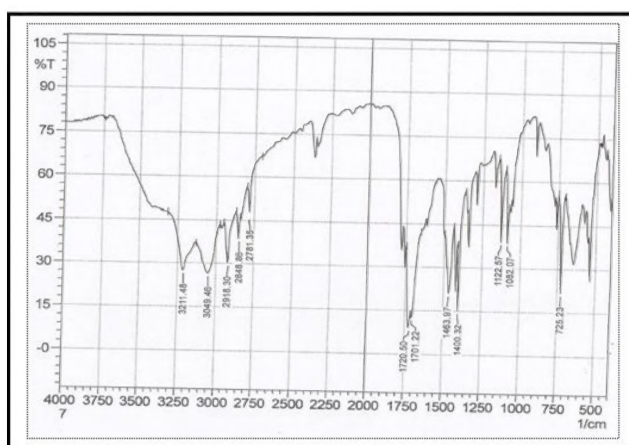
Figures (7-9) show the IR spectra of the polymers and copolymers respectively while Table 1 summarized the important vibration bands of the prepared complexes, the observed vibration bands are similar to those in the literature.

The IR spectra show a strong band in the range  $(1400-1463)\text{cm}^{-1}$  due to  $(\text{C} = \text{C})$  stretching<sup>[9,10]</sup> while  $(\text{C} = \text{N})$  stretching appear in the range  $(1637-1691)\text{cm}^{-1}$ .

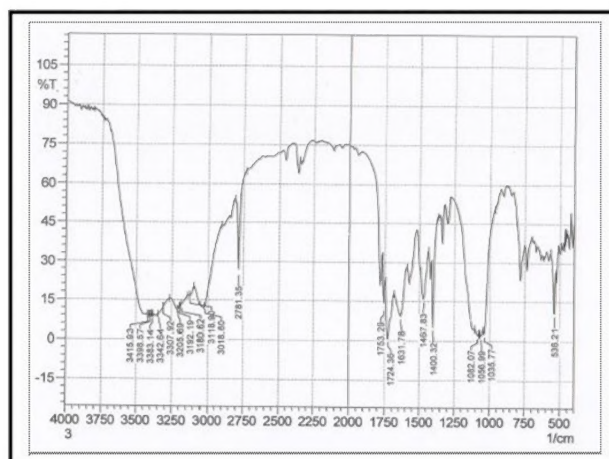
The aromatic C-H stretching band appeared in the range  $(3048-3140\text{cm}^{-1})$  and the bands in the range  $(536-590\text{cm}^{-1})$  which might be attributed to the stretching vibration of the (M-F) band. These bands refer to the bridging structures of those polymer.

**Table 1: The I. R- Absorption Data for the Prepared Complexes**

Compounds	C-H (st)	C = C (st)	C = N (st)	C-N (st)	Al-F (st)	C-H <sub>ben</sub>	
						Out Plane	In the Plane
(AlPC-F) <sub>n</sub>	3211 3049	1400 1463	1650 1691	1300 1350	620	725	1082 1122
(AlPzF) <sub>n</sub>	3140	1400	1662	1300	590	750	1035 1060 1068
Copolymer (PCAIF- ALPzF) <sub>n</sub>	3018	1400	1631	1300- 1350	536	745 755	1035 1056 1082



**Figure 7: The IR Spectrum of (AL PCF)<sub>n</sub>**



**Figure 8: The IR Spectrum of (ALPzF)<sub>n</sub>**



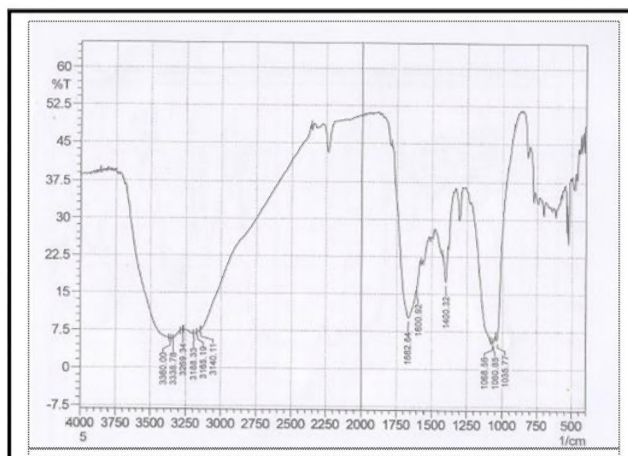


Figure 9: The IR Spectrum of the Copolymer

## ELECTRONIC SPECTRA

The uv-visible data of all prepared complex are measured in the range (200-800nm) using DMF as solvent and they are summarized in the table 2. Two electronic transition are observed in all spectra. The first transition was observed in the range (610-670nm) which is can be attributed to a Q-band. The second band which observed in the range (320-345nm) can be attributed to a B-band (Sort-band). These bands are due to ( $\pi - \pi$ )<sup>[10, 11]</sup> and (n -  $\pi$ ) transitions which belong to the hetro-aromatic system of the phthalocyanine and tetrapyrzino porphyrazine molecules..

Table 3: Show the Absorption Bands to the Prepared Compounds

Compounds	Q-Band nm	B-Band nm
Al Pc Cl	610	350
( AL PcF) <sub>n</sub>	670	340
Al PzCl	620	340
(AlPzF) <sub>n</sub>	660	345
Copolymer (AlPCF- AlPzF) <sub>n</sub>	610	320

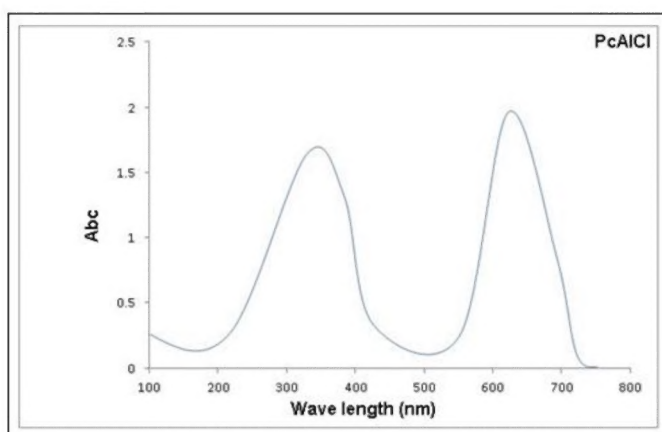


Figure 10: The Uv-Visible Spectrum of Al Pc Cl

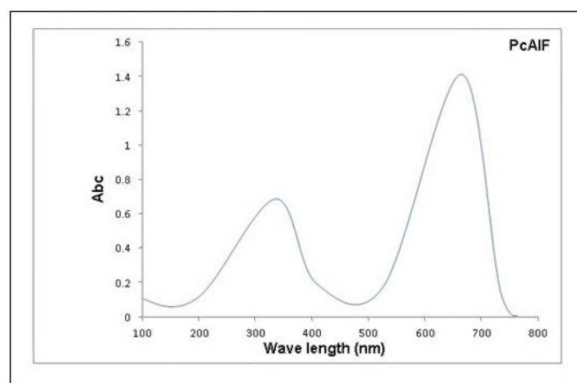


Figure 11: The UV-Visible of  $(Al\ PcF)_n$

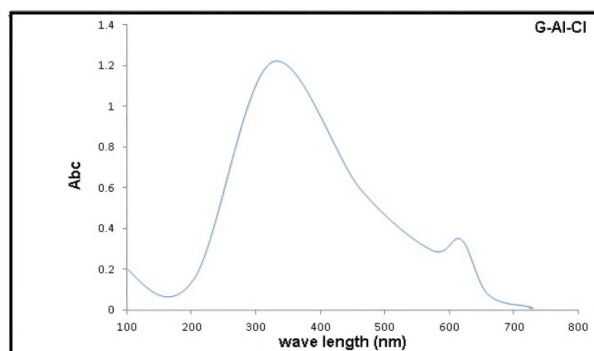


Figure 12: The UV-Visible Spectrum of  $Al\ PzCl$

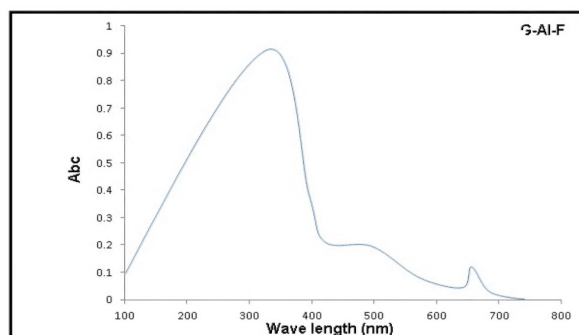


Figure 13: The UV-Visible Spectrum of  $(AlPzF)_n$

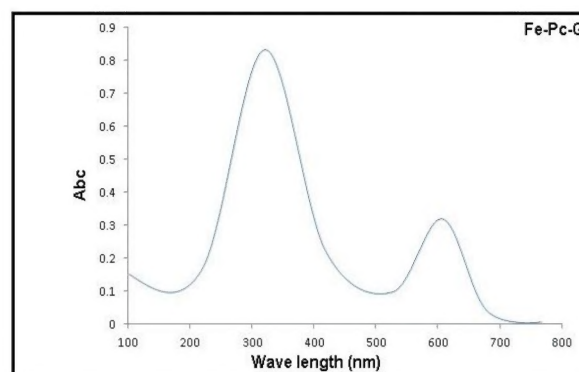
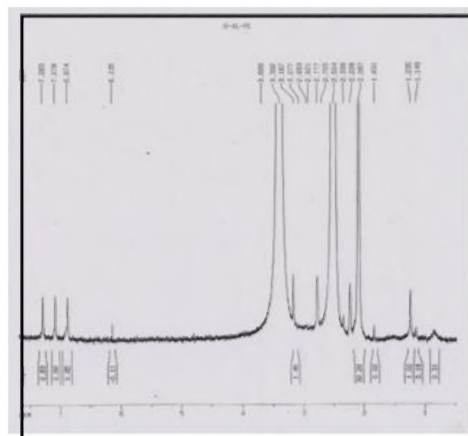
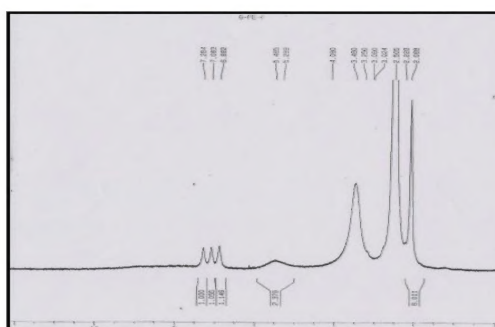
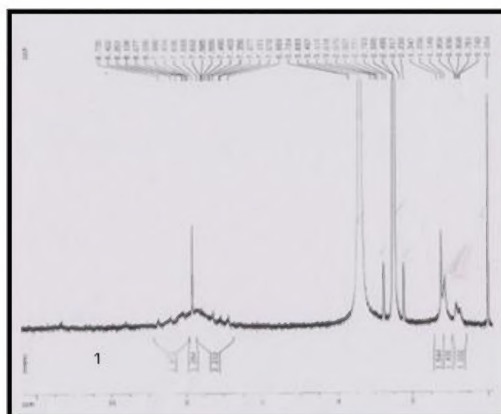


Figure 14: The UV-Visible Spectrum of the Copolymer

The spectra show DMSO peaks at 2.2ppm and 2.4 ppm for (AlPcF)<sub>n</sub>, 2.08 ppm, 2.5 ppm for (AlPzF)<sub>n</sub> and at 2.08 ppm, 2.5 ppm for the copolymer. The DMSO moisture shows peaks at 3.4ppm for (AlPcF)<sub>n</sub>, 3.4ppm and 5.2ppm for (AlPzF)<sub>n</sub> and 3.3ppm for the copolymer respectively.<sup>[11]</sup>





## REFERENCES

1. G. Erqun; *J. Flourine chem.*, 14, 65-71(2013).
2. S. L. J. Michel, S. Baum, A. G. M. Barrett and B. M. Hoffman "Progress in Inorganic chemistry" Wiley: New York(2001).
3. F. H. Moser and A.L. Thomas; "Phthalocyanine compounds" Reinhold publishing corporation; new York(1963).
4. P. S. Sesaham, A. Koca and A. Gul; *Bayhedron*, 22, 3083(2003).
5. J. Simon and J. J. Andr'e; "Organic Semiconductors" John and Willy, London (1985).
6. M. Hanack; R. Polley and S. Deser; *Synth. Mat.*; 110, 93(2000).
7. M. Hanack and U. Keppeir; *Chem. Ber.*; 119, 3368(1986).
8. J. P. Linsky and T. R. Pull; *Inorg. chem.*, 19, 3131, (1980).
9. S. Higuchi, M. Futamata and S. Takahashi; *Synth. Mat.*; 30, 39(1989).
10. A. Maciej, R. Srinivasa, J. Ponal and R. Thnam; *Tetrahedron*, 59, 8129(2003).
11. H. Akkuf and A. Gul; *Trans. Met, Chem.*; 26, 689(2001).
12. B. H. Lee, J. Y. Jung and S. C. Bezza; *Dyes and Pigments*; 65, 159(2005).
13. M. P. Dozello, C. Frcolan and P. A. Stuzhim; *Coordination chemistry Reviews*; 250, 1530(2006).
14. M. P. P Donzello. *Inorg. Chem.*; 43, (26)8626(2004).
15. K. Kopecky, P. Zimicik, V. Novakova, M. Mileitein, Z. Musil and J. Stribna; *Dyes and Pigments*, 78,213(2008).

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1. G. Erqun ; *J. Flourine chem.*, 14, 65-71(2013).
  2. S. L. J. Michel, S. Baum, A.G.M.Barrett and B.M.Hoffman"Progress in Inorganic chemistry" Wiley: New York(2001).
  3. F. H. Moser and A.L. Thomas ; "Phthalocyanine compounds" Reinhold publishing corporation; new York(1963).
  4. P.S. Sesaham, A. Koca and A. Gul; *Bayhedron*, 22,3083(2003).
  5. J. Simon and J.J. Andr'e; "Organic Semiconductors" John and Willy, London(1985).
  6. M. Hanack; R. Polley and S. Deser; *Synth. Mat.*; 110, 93(2000).
  7. M. Hanack and U. Keppeir; *Chem. Ber.*; 119, 3368(1986).
  8. J. P. Linsky and T. R. Pull; *Inorg. chem.*, 19, 3131,(1980).
  9. S. Higuchi, M. Futamata and S. Takahashi; *Synth. Mat*; 30, 39(1989).
  10. A. Maciej, R. Srinivasa, J. Ponal and R. Thnam; *Tetrahedron*, 59, 8129(2003).
  11. H. Akkuf and A. Gul; *Trans. Met, Chem.*; 26,689(2001).
  12. B. H. Lee, J. Y. Jung and S. C. Bezza; *Dyes and Pigments*; 65, 159(2005).
  13. M. P. Dozello, C. Frcolan and P. A. Stuzhim; *Coordination chemistry Reviews*; 250, 1530(2006).
  14. M. P. P Donzello. *Inorg. Chem.*; 43, (26)8626(2004).
  15. K. Kopecky, P. Zimicik , V. Novakova, M. Mileitein, Z. Musil and J. Stribna; *Dyes and Pigments*, 78,213(2008).

